

# IONIC EQUILIBRIUM-III |

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## 9.1 INTRODUCTION

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In the previous two units on ionic equilibrium you have learnt about the nature of electrolytes, theories of acids and bases, concept of pH, behaviour of weak acids and bases including diprotic and polyprotic acids, common ion effect and buffer solutions. You have also learnt about calculating the pH of aqueous solutions of acids, bases and buffer solutions. In this last unit of the block we would continue our discussion on ionic equilibrium and would take up the hydrolysis of different types of salts and solubility equilibria of sparingly soluble salts.

In the context of hydrolysis of salts we would discuss the meaning of hydrolysis and define the term, ‘degree of hydrolysis’. This would then be used to qualitatively predict the acid-base nature of the salt solutions. Thereafter, the hydrolysis equilibrium would be characterised in terms of hydrolysis constant and will be related to the acid/ base ionisation constants of the conjugate acid/base of the ions getting hydrolysed. We would also work out the expressions for calculating the pH of the aqueous solutions of different types of salts.

The discussion on hydrolysis of salts would be followed by the equilibria associated with the solubility of sparingly soluble salts. In this context we

would introduce the concept of solubility product constant and relate it to the solubility for different types of salts. The effect of common ions and of the solution pH on the solubility equilibrium and hence the solubility would also be taken up. Towards the end of the unit we would take up important qualitative and quantitative applications of solubility product principle.

In the next block of this course you would learn about preparation of aromatic compounds.

## Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ explain the hydrolysis behaviour of different types of salts;
- ❖ differentiate between the hydrolysis behaviour of acidic, basic and neutral salts;
- ❖ predict whether an aqueous solution of a given salt would be acidic, basic or neutral;
- ❖ define degree of hydrolysis and hydrolysis constant, and derive a relationship between them;
- ❖ derive expressions for calculating the pH of aqueous solutions of different types of salts;
- ❖ calculate the pH of aqueous solutions of different types of salts;
- ❖ define solubility and express the solubility equilibrium of sparingly soluble salts in terms of suitable expressions;
- ❖ derive the relationship between solubility and solubility product constant for salts of AB, AB<sub>2</sub>, A<sub>2</sub>B and A<sub>2</sub>B<sub>3</sub> types;
- ❖ explain the effect of common ion on solubility equilibrium of sparingly soluble salts;
- ❖ discuss the effect of pH on the solubility of sparingly soluble salts; and
- ❖ discuss some quantitative and qualitative applications of solubility product principle.

## 9.2 SALT HYDROLYSIS

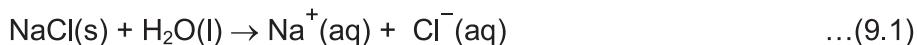
As you are aware, that salts are produced as a result of neutralisation reaction between an acid and a base. What would be the acid-base nature of the aqueous solutions prepared from these salts? Will they be acidic, basic or neutral? Let's check!

Let's take 100 cm<sup>3</sup> of distilled water each in three beakers labelled as 1,2 and 3 and add 0.5 g of sodium chloride to beaker labelled as 1, 0.5 g of sodium acetate to beaker labelled as 2 and 0.5 g of ammonium chloride to beaker labelled as 3. If we measure the pH of the resulting solutions at 298 K, we find that the solution of sodium chloride has a pH of 7.0; the pH of ammonium

chloride is in acidic range whereas that of sodium acetate solution is found to be in basic range. The question comes up is “why do different salt solutions have different acid-base behaviour?” To understand this let’s analyse the behaviour of the ions produced when these salts are dissolved in water.

### Dissolution of Sodium Chloride

On dissolving sodium chloride in water, the water molecules hydrate the ions in the lattice of the salt and as a result of the energy released in the process the ions dissociate from the lattice and are released in the solution. The overall process can be given as



The ions so produced ( $\text{Na}^+$  and  $\text{Cl}^-$ ) do not react with water and move freely in solution.



Let’s learn why don’t these ions react with water? You would recall the ionisation of hydrochloric acid in water is given as



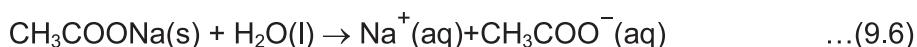
Here, water molecules accept a proton from HCl and form hydronium ions. As hydrochloric acid is a strong acid, the reaction goes to completion in the forward direction i.e., there is no backward reaction. You may note that in this reaction, there are two bases viz.,  $\text{H}_2\text{O}$  and  $\text{Cl}^-$  ions. Since the reaction does not go in backward direction i.e., here the chloride ions do not accept a hydrogen ion to form HCl; we can say that  $\text{Cl}^-$  ion (anion of strong acid, HCl) is much weaker a base than  $\text{H}_2\text{O}$  and does not react with it. That explains the reaction in Eq. (9.3). Similarly, we can consider the ionisation of NaOH which can be shown as



Here again the reaction goes to completion in the forward direction. This implies that sodium ions (cations of a strong base) are much weaker an acid than water and do not react with it. As both ( $\text{Na}^+$  and  $\text{Cl}^-$ ) the ions do not react with water the solution is neutral as it contains equal number of hydronium and hydroxide ions from autoprotolysis of water. Such salts are called **neutral salts**.

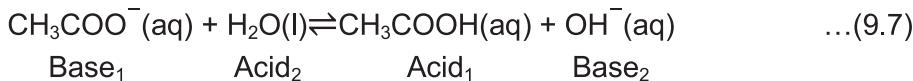
### Dissolution of Sodium Acetate

On dissolution of sodium acetate in water the ions in the lattice are hydrated and are dissociated from the lattice due to the energy released during their hydration. The overall process can be given as



The reactions of ions ( $\text{Na}^+$  and  $\text{CH}_3\text{COO}^-$ ) so produced with water are as under

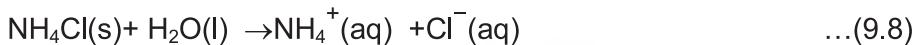
The anion of a strong acid is a much weaker base than  $\text{H}_2\text{O}$  and does not react with water.



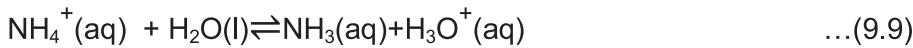
Here, the acetate ions accept hydrogen ion from water and act as a base as per Brønsted-Lowry concept. In other words, the anion ( $\text{CH}_3\text{COO}^-$ ) of weak acid ( $\text{CH}_3\text{COOH}$ ) acts as a stronger base as compared to water. Secondly, as before, the cation ( $\text{Na}^+$ ) of a strong base ( $\text{NaOH}$ ) does not react with water. As the reaction produces  $\text{OH}^-$  ions, the resulting solution is basic and the pH is more than 7 at 298 K. Such salts are called **basic salts**.

### Dissolution of Ammonium Chloride

On dissolution of ammonium chloride in water the ions in the lattice are hydrated and are dissociated from the lattice due to the energy released during their hydration. The overall process can be given as



The reactions of ions ( $\text{NH}_4^+$  and  $\text{Cl}^-$ ) so produced with water are as under



Here, the ammonium ions donate hydrogen ion to water and act as an acid as per Brønsted-Lowry concept. In other words, the cation of a weak base acts as a stronger acid than water. As the reaction produces  $\text{H}_3\text{O}^+$  ions, the resulting solution is acidic and hence the pH is less than 7 at 298 K. Secondly, as before the anion ( $\text{Cl}^-$ ) of a strong acid ( $\text{HCl}$ ) does not react with water.

In the process of dissolution of a salt in water, the solvent molecules hydrate the ions in the lattice and the energy so released overcomes the lattice energy binding the ions together. As a result the solvated ions dissociate from the lattice and come into the solution as solvated (hydrated here) ions.

In these examples we have seen the behaviour of different ions in aqueous solutions. Of the four ions taken up, we find that two ( $\text{CH}_3\text{COO}^-$  and  $\text{NH}_4^+$ ) of these ions do react with water. This reaction of anions or/and cations produced by the salts with water is called **salt hydrolysis**. You may note here that the anions of weak acids produce the conjugate acid and hydroxide ion whereas the cations of weak bases give the conjugate base and hydronium ion on reaction with water. Accordingly, the resulting solution is basic or acidic respectively. Now the question is that, "What would be the nature of solution obtained by dissolving  $\text{NH}_4\text{NO}_2$ — a salt of a weak acid and a weak base in water?" Write your response here before you move ahead.

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You know that  $\text{NH}_4\text{NO}_2$  is formed by neutralization of a weak acid ( $\text{HNO}_2$ ) by a weak base ( $\text{NH}_4\text{OH}$ ). Therefore, you are right to think that in this case both, the anion as well the cation produced on dissolution of  $\text{NH}_4\text{NO}_2$  would undergo hydrolysis. The acid-base nature of this solution would then be determined by the relative amounts of the hydronium and hydroxide ions produced in solution due to their hydrolysis. We would discuss the basis to answer this question in the next subsection.

## 9.2.1 Hydrolysis Constants and Degree of Hydrolysis

In order to learn about quantitative aspects of the salt hydrolysis, let us take up the equilibrium given in Eq. (9.7). This reaction represents the hydrolysis of acetate ions.



In this reaction Eq. (9.7) acetate ion behaves as a weak base and the equilibrium can be seen as for the ionisation of a weak base and the equilibrium constant can be seen as  $K_b$  –the ionisation constant for the weak base

$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

As the equilibrium in this reaction concerns the *hydrolysis* of an ion it can be called as **hydrolysis equilibrium** and the equilibrium constant characterising it is called **hydrolysis constant**,  $K_h$ . The hydrolysis constant expression for the reaction in Eq. (9.7) would be

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \quad \dots(9.10)$$

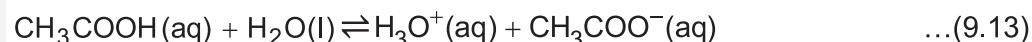
Let's multiply the numerator and denominator of the Eq. (9.10) by the concentration of hydronium ions,  $[\text{H}_3\text{O}^+]$ .

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]} \quad \dots(9.11)$$

On reorganising the terms, we get

$$K_h = \left( \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]} \right) \times ([\text{OH}^-][\text{H}_3\text{O}^+]) \quad \dots(9.12)$$

Don't you find the first and second terms in Eq. (9.12) familiar? Let's recall the ionisation of acetic acid in water and the corresponding ionisation constant



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad \dots(9.14)$$

You can note that the first term on the right hand side in Eq. (9.12) is the reciprocal of the expression in Eq. (9.14). Further, the second term in the Eq. (9.12) is nothing but the  $K_w$ , the ionic product of water. Substituting these into Eq. (9.12) we get an important relation.

$$K_h = \left( \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]} \right) \times ([\text{OH}^-][\text{H}_3\text{O}^+]) = \frac{1}{K_a} \times K_w \quad \dots(9.15)$$

$$K_h = \frac{K_w}{K_a} \text{ or } K_a K_h = K_w \quad \dots(9.16)$$

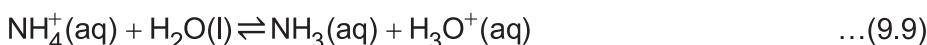
This implies that the product of  $K_h$  of the anion acting as a base and  $K_a$  of its conjugate acid equals ionic product of water ( $K_w$ ). You may take note from Eq.(9.15) that the hydrolysis constant ( $K_h$ ) of the anion of a salt varies inversely as the ionisation constant  $K_a$  of the corresponding conjugate acid. That is, *weaker the acid, greater is the hydrolysis constant of its anion*.

If we replace  $K_h$  in Eq. (9.16) by  $K_b$

$$K_a K_b = K_w$$

we can say that for conjugate acid–base pairs the product of acid- and base- ionisation constants in aqueous solution equals the ionic product constant of water.

Similarly, we can consider the hydrolysis equilibrium given in Eq.(9.9) wherein ammonium ions hydrolyse by donating a hydrogen ion(act as a weak acid) to water.



The expression for hydrolysis constant would be as follows

$$K_h = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} \quad \dots(9.17)$$

Again by multiplying the numerator and the denominator of the expression by concentration of hydronium ions,  $[\text{H}_3\text{O}^+]$  and reorganising the terms as before, we would get

$$\Rightarrow K_h = \frac{K_w}{K_b} \quad \text{or} \quad K_h K_b = K_w \quad \dots(9.18)$$

This implies that the product of  $K_h$  of the cation acting as a weak acid and  $K_b$  of its conjugate base equals ionic product of water ( $K_w$ ). Further, the hydrolysis constant ( $K_h$ ) of the cation of a salt of a weak base varies inversely as the dissociation constant,  $K_b$ , of the corresponding conjugate base. Having learnt about hydrolysis and its quantitative expression, let us define the term, ‘degree of hydrolysis’ and develop a relationship between the hydrolysis constant and degree of hydrolysis of an ion.

In this reaction (Eq. 9.9) ammonium ion behaves as a weak acid and the equilibrium can be seen as for the ionisation of a weak acid and the equilibrium constant can be seen as  $K_a$  –the ionisation constant for the weak acid

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{\text{NH}_4^+}$$

### Degree of Hydrolysis

We can define a parameter called ‘degree of hydrolysis’ that is similar to the degree of ionisation or degree of dissociation defined in previous unit. This refers to the extent of hydrolysis or *the fraction of the anions of weak acids or cations of weak base in solution that react with water and get hydrolysed*. Like degree of ionisation or dissociation, the degree of hydrolysis is also represented in terms of Greek alphabet  $\alpha$  (Some people prefer to use  $h$  or  $x$  as a symbol for the degree of hydrolysis; however we would use  $\alpha$ ). Let us consider the hydrolysis of an anion,  $\text{A}^-$  of the weak acid HA, taken in aqueous solution.



If we take a salt solution containing  $c \text{ mol dm}^{-3}$  of the anion,  $\text{A}^-$  of the weak acid HA, and assume that the degree of hydrolysis of the anion at this concentration is ‘ $\alpha$ ’; then the initial and equilibrium concentrations of different species in the solution would be as follows

Concentration / mol dm <sup>-3</sup>	$\text{A}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HA}(\text{aq}) + \text{OH}^-(\text{aq})$		
Initial	$c$	0	0
Change due to hydrolysis	$-c\alpha$	$c\alpha$	$c\alpha$
At equilibrium	$c(1-\alpha)$	$c\alpha$	$c\alpha$

The equilibrium constant for the hydrolysis reaction for the anion can be written as

$$K_h = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \quad \dots(9.20)$$

You may note here that the same expression, Eq. (9.21), would be valid for the hydrolysis of the cation of a weak base.

Substituting the concentrations of different species at equilibrium, from the table above, in Eq. (9.20) we get,

$$K_h = \frac{c\alpha \times c\alpha}{c(1-\alpha)} \Rightarrow K_h = \frac{c\alpha^2}{(1-\alpha)} \quad \dots(9.21)$$

Assuming that  $\alpha$ , is small as compared to 1, we can ignore it in the denominator of Eq. (9.21), we get

$$K_h = c\alpha^2 \quad \alpha = \sqrt{\frac{K_h}{c}} \quad \dots(9.22)$$

Recall from Eq. (9.16),

$$K_h = \frac{K_w}{K_a} \quad \dots(9.16)$$

Substituting it in Eq.(9.22) we get,

$$\alpha = \sqrt{\frac{K_w}{K_a c}} \quad \dots(9.23)$$

Thus, knowing the values of  $K_w$ ,  $K_a$  and the concentration of the anion we can calculate its degree of hydrolysis. Similarly we can derive a relationship between the degree of hydrolysis of a cation of a weak base and the ionisation constant of the weak base. The relationship would be

$$\alpha = \sqrt{\frac{K_w}{K_b c}} \quad \dots(9.24)$$

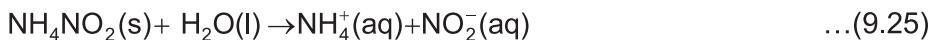
Having learnt about the degree of hydrolysis of ions and their relationship with the acid/base dissociation constants of the conjugate acid/base we can now take up the question raised just before the beginning of the subsection 9.2.1. Recall that we asked for the acid-base nature of solution obtained by dissolving  $\text{NH}_4\text{NO}_2$  in water. Let's take it as an example now and calculate the degree of hydrolysis of the ions obtained on its dissolution so as to check the acid-base nature of the aqueous solution of  $\text{NH}_4\text{NO}_2$ .

You may derive the relationship given in Eq. (9.24) in the same way.

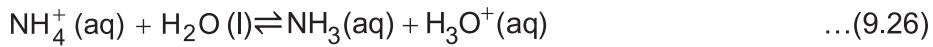
**Example 9.1:** Determine the acid-base nature of the aqueous solution obtained by dissolving  $\text{NH}_4\text{NO}_2$  in water to get 0.01 M solution at 298 K.

[Given  $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$ ;  $K_a(\text{HNO}_2) = 4.5 \times 10^{-4}$ ]

**Solution:** The dissolution of ammonium nitrite in water involves the hydration of the ions and their dissociation from the lattice. The overall process can be given as



The reactions of the ions ( $\text{NH}_4^+$  and  $\text{NO}_2^-$ ) so produced with water are as under



In water ammonia exists as ammonium hydroxide ( $\text{NH}_4\text{OH}$ )

The degree of hydrolysis of ammonium ions would be given by Eq. (9.24)

$$\alpha = \sqrt{\frac{K_w}{K_b c}} \quad \dots(9.24)$$

where  $K_b$  is the base ionisation constant for the conjugate base ( $\text{NH}_4\text{OH}$ ) of ammonium ion. Substituting the values at 298 K, we get

$$\Rightarrow \alpha = \sqrt{\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 10^{-2}}} = \sqrt{5.55 \times 10^{-8}} = 2.36 \times 10^{-4}$$

On the other hand the degree of hydrolysis of nitrite ions would be given by Eq. (9.23).

$$\alpha = \sqrt{\frac{K_w}{K_a c}} \quad \dots(9.23)$$

where  $K_a$  is the acid ionisation constant for the conjugate acid  $\text{HNO}_2$ .

Substituting the values at 298 K, we get

$$\Rightarrow \alpha = \sqrt{\frac{1.0 \times 10^{-14}}{4.5 \times 10^{-4} \times 10^{-2}}} = \sqrt{2.22 \times 10^{-9}} = 4.7 \times 10^{-5}$$

So we see that the degree of hydrolysis of ammonium ions that produce hydronium ions is more than that of nitrite ions which generate hydroxide ions. This means that in the solution the concentration of hydronium ions will be more than that of the hydroxide ions. ***Therefore the solution would be acidic and would have a pH value of less than 7.0 at 298 K.***

We have discussed about the acid-base nature of aqueous solutions of different types of salts on the basis of degree of hydrolysis. We can even work out mathematical equations for calculating the pH of salt solutions. However before we derive these equations solve the following SAQ to assess your understanding of the hydrolysis of salts.

### SAQ 1

Define salt hydrolysis and calculate the degree of hydrolysis of benzoate ions in 0.01M aqueous solution of sodium benzoate at 298 K.

[Given:  $K_a(\text{C}_6\text{H}_5\text{COOH}) = 6.5 \times 10^{-5}$  at 298 K]

**SAQ 2**

In the salts listed in the first column of the table given below, write the ion (s) that will be hydrolysed in the column 2 and the acid-base nature of the salt in the column 3 respectively.

Given:  $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$ ;  $K_a(\text{HCOOH}) = 1.8 \times 10^{-4}$ ;  
 $K_a(\text{C}_6\text{H}_5\text{COOH}) = 6.5 \times 10^{-5}$

Salt	Ion (s) that will be hydrolysed	Acid-base nature of the resulting aqueous solution of the salt
HCOONa		
NH <sub>4</sub> Br		
C <sub>6</sub> H <sub>5</sub> COONH <sub>4</sub>		

### 9.3 pH OF SALT SOLUTIONS

You have so far learnt that when salts dissolve in water the ions present in the lattice get hydrated and dissociate from the lattice. Thereafter, in some cases the ions react with water molecules to either donate a hydrogen ion to it or accept a hydrogen ion from it and in the process act as an acid or a base. This produces hydronium or hydroxide ions and makes the solution acidic or basic respectively. Let's learn how to calculate the pH of such salt solutions. We would take four cases as:

- a) Aqueous solution of salt of a strong acid and a strong base
- b) Aqueous solution of salt of a weak acid and a strong base
- c) Aqueous solution of salt of a strong acid and weak base
- d) Aqueous solution of salt of a weak acid and a weak base

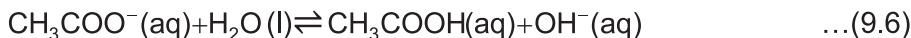
Let's begin with aqueous solution of salt of a strong acid and a strong base.

**a) pH of aqueous solution of salt of a strong acid and a strong base**

You would recall from above in section 9.2 that when a salt of a strong acid and a strong base e.g., NaCl dissolves in water the resulting ions do not react with water. That is, neither the anion nor the cation gets hydrolysed. In such a case the only source of hydronium and hydroxide ions in the solution is the autoprotolysis of water. As this process generates equal amounts of the hydronium and hydroxide ions so the resulting solution is neutral and has a pH of 7.0 at 298K.

**b) pH of aqueous solution of salt of a weak acid and a strong base**

Once again, as discussed above in section 9.2 when a salt of a weak acid and a strong base dissolves in water, the resulting cation remains unaffected and it is the anion that gets hydrolysed. For example, in case of dissolution of sodium acetate, the acetate ( $\text{CH}_3\text{COO}^-$ ) ions react with water as under and get hydrolysed.



You have learnt above that if we start with a solution containing  $c$  mol dm<sup>-3</sup> of the anion of the weak acid and assume that the degree of hydrolysis of the anion at this concentration to be  $\alpha$ , then the hydrolysis constant is given as

$$K_h = \frac{c\alpha \times c\alpha}{c(1-\alpha)} \quad \dots(9.21)$$

and the equilibrium concentration of hydroxide ions obtained from hydrolysis is equal to  $c\alpha$ . Rearranging Eq. (9.21) and ignoring  $\alpha$  in the denominator we get

$$cK_h = c^2\alpha^2 = [\text{OH}^-]^2$$

$$\Rightarrow [\text{OH}^-] = \sqrt{cK_h} \quad \dots(9.28)$$

$$\text{You know that, } [\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$$

Substituting from Eq. (9.28)

$$\Rightarrow [\text{H}_3\text{O}^+] = \frac{K_w}{\sqrt{cK_h}} = \sqrt{\frac{K_w^2}{cK_h}} \quad \dots(9.29)$$

Further, from Eq. (9.16),

$$\Rightarrow K_h = \frac{K_w}{K_a}$$

Substituting in Eq. (9.29) we get

$$\Rightarrow [\text{H}_3\text{O}^+] = \sqrt{\frac{K_w^2}{cK_h}} = \sqrt{\frac{K_w^2 K_a}{cK_w}} \quad \dots(9.30)$$

Simplifying,

$$\Rightarrow [\text{H}_3\text{O}^+] = \sqrt{\frac{K_w K_a}{c}} \quad \dots(9.31)$$

Taking logarithm on both sides, we get

$$\log[\text{H}_3\text{O}^+] = \frac{1}{2}(\log K_w + \log K_a - \log c) \quad \dots(9.32)$$

Multiplying throughout by  $-1$

$$-\log[\text{H}_3\text{O}^+] = -\frac{1}{2}\log K_w - \frac{1}{2}\log K_a + \frac{1}{2}\log c \quad \dots(9.33)$$

$$\text{pH} = \frac{1}{2}\text{p}K_w + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log c \quad \dots(9.34)$$

We know that at 298 K,  $\text{p}K_w = 14.0$  at 298K

$$\Rightarrow \text{pH} = \frac{1}{2}(14) + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log c \quad \dots(9.35)$$

$$\Rightarrow \text{pH} = 7.0 + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log c \quad \dots(9.36)$$

This is the desired expression for calculating the pH of an aqueous solution prepared by dissolving a salt of a weak acid with a strong base in water. You may note here that the second term in the Eq. (9.36) is positive and the third term is slightly negative at moderate concentrations; the resulting solution would have a pH > 7.0 i.e., the solution would be basic.

You may say that in highly dilute solutions (say  $c < 10^{-5}$  M), the third term may become larger than the second term and the pH may become less than 7.0. Here you must remember that at such low concentrations the autoprotolysis of water would become important and the concentration of hydroxyl ions from that could not be neglected and the pH would be close to 7 but the solution would remain basic.

**Example 9.2:** Calculate the pH of 0.01 M aqueous solution of sodium acetate at 298 K. [Given:  $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$  at 298K]

**Solution:** As sodium acetate is a salt of a weak acid and a strong base the pH of its aqueous solution would be given by the Eq. (9.36).

$$\Rightarrow \text{pH} = 7.0 + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log c \quad \dots(9.36)$$

Let's first calculate the  $\text{p}K_a$  for acetic acid (the conjugate acid of the anion)

$$\text{p}K_a = -\log K_a = -\log(1.8 \times 10^{-5}) = -(-4.74) = 4.74$$

Substituting the values of  $\text{p}K_a$  and  $c$  in Eq. (9.36)

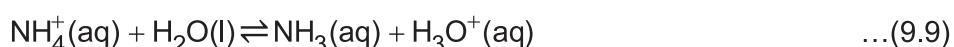
$$\Rightarrow \text{pH} = 7.0 + \frac{1}{2}(4.74) + \frac{1}{2}\log(1.0 \times 10^{-2})$$

$$\Rightarrow \text{pH} = 7.0 + 2.37 + \frac{1}{2}(-2.0) = 9.37 - 1.0 = 8.37$$

Thus, the pH of 0.01 M aqueous solution of sodium acetate would be 8.37.

### c) pH of aqueous solution of salt of a weak base and a strong acid

Recall from Sec. 9.2 that when a salt of a weak base and a strong acid dissolves in water, the resulting anion remains unaffected and it is the cation that gets hydrolysed. For example, in case of dissolution of ammonium chloride, the ammonium ( $\text{NH}_4^+$ ) ions react with water and get hydrolysed as under.



You have also learnt above that for a  $c \text{ mol dm}^{-3}$  aqueous solution of a cation of the weak base if we assume the degree of hydrolysis to be  $\alpha$  the hydrolysis constant of the cation is given as

$$K_h = \frac{c\alpha \times c\alpha}{c(1-\alpha)} \quad \dots(9.21)$$

and the concentration of the resulting hydronium ions is equal to  $c\alpha$ .

Rearranging Eq. (9.21) and ignoring  $\alpha$  in the denominator we get

$$cK_h = c^2\alpha^2$$

Substituting  $c\alpha$  by  $[\text{H}_3\text{O}^+]$

$$cK_h = [\text{H}_3\text{O}^+]^2$$

$$\Rightarrow [\text{H}_3\text{O}^+] = \sqrt{cK_h} \quad \dots(9.37)$$

Further, from Eq. (9.18),

$$\Rightarrow K_h = \frac{K_w}{K_b}$$

Substituting in Eq. (9.37), we get

$$\Rightarrow [\text{H}_3\text{O}^+] = \sqrt{\frac{cK_w}{K_b}} \quad \dots(9.38)$$

Taking logarithm on both sides, we get

$$\log[\text{H}_3\text{O}^+] = \frac{1}{2}\log K_w - \frac{1}{2}\log K_b + \frac{1}{2}\log c \quad \dots(9.39)$$

Multiplying throughout by  $-1$

$$-\log[\text{H}_3\text{O}^+] = -\frac{1}{2}\log K_w + \frac{1}{2}\log K_b - \frac{1}{2}\log c \quad \dots(9.40)$$

$$\text{pH} = \frac{1}{2}\text{p}K_w - \frac{1}{2}\text{p}K_b - \frac{1}{2}\log c \quad \dots(9.41)$$

We know that,  $\text{p}K_w$  (at 298 K) = 14.0, substituting in Eq. (9.41)

$$\Rightarrow \text{pH} = 7.0 - \frac{1}{2}\text{p}K_b - \frac{1}{2}\log c \quad \dots(9.42)$$

This is the desired expression for the pH of an aqueous solution prepared by dissolving a salt of a weak base with a strong acid in water at 298 K.

Remember that this equation is valid only at 298 K. At any other temperature the first term on the right would be different. Let us take an example to see the application of this expression.

**Example 9.3:** Calculate the pH of 0.001 M aqueous solution of ammonium chloride at 298 K. [Given:  $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$ ]

**Solution:** As ammonium chloride is a salt of a weak base with a strong acid its pH would be given by Eq. (9.42)

$$\Rightarrow \quad \text{pH} = 7.0 - \frac{1}{2}\text{p}K_b - \frac{1}{2}\log c \quad \dots(9.42)$$

Let's first calculate the  $\text{p}K_b$  for ammonium hydroxide (the conjugate base of the cation)

$$\text{p}K_b = -\log K_b = -\log [1.8 \times 10^{-5}] = -[-4.74] = 4.74$$

Substituting the values of  $\text{p}K_b$  and  $c$  in the Eq. (9.42)

$$\Rightarrow \quad \text{pH} = 7.0 - \frac{1}{2}(4.74) - \frac{1}{2}\log(1.0 \times 10^{-3})$$

$$\Rightarrow \quad \text{pH} = 7.0 - 2.37 - \frac{1}{2}(-3.0) = 4.63 + 1.50 = 6.13$$

Thus, the pH of 0.001 M aqueous solution of ammonium chloride at 298 K would be 6.13 i.e., the solution would be acidic.

#### d) pH of aqueous solution of salt of a weak acid and a weak base

On the basis of what you have learnt so far in this unit you understand that when a salt of a weak acid and a weak base dissolves in water the resulting anion as well as the cation would get hydrolysed. Let us consider a salt BA that dissociates to give the ions  $B^+$  and  $A^-$  both of which get hydrolysed. The overall reaction of hydration and dissociation of the salt can be represented as



Here, both the ions would get hydrolysed. Though their concentrations would be same but the degree of their hydrolysis would depend on the magnitude of the ionisation constants of the corresponding conjugate acid/base. In other words, we may say that the pH of the solution would depend on the values of  $K_a$ , the acid dissociation constant of the conjugate acid of the anion as well as  $K_b$ , the base dissociation constant of the conjugate base of the cation. The exact treatment of the equilibria involved in this case is quite complex and beyond the scope of this course. However we can learn about the resulting expression and analyse the same. The expression for the pH of an aqueous solution prepared by dissolving the salt of a weak acid with a weak base in water at 298 K is as follows.

$$\text{pH} = 7.0 + \frac{1}{2}\text{p}K_a - \frac{1}{2}\text{p}K_b \quad \dots(9.44)$$

You may note a few things here. First, as expected the pH depends on the  $\text{p}K_a$  as well as the  $\text{p}K_b$ . Secondly, the pH does not depend on the concentration of the salt and thirdly, if the  $\text{p}K_a = \text{p}K_b$ , then the solution would be neutral and at

298 K the pH would be 7.0. In order to see the application of this expression let us take up the problem in the example 9.1 once again.

**Example 9.4:** Calculate the pH of a 0.01 M aqueous solution of  $\text{NH}_4\text{NO}_2$  at 298 K. [Given:  $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$ ;  $K_a(\text{HNO}_2) = 4.5 \times 10^{-4}$ ]

**Solution:** As ammonium nitrite is a salt of a weak acid and a weak base its pH would be given by Eq. (9.44).

$$\text{pH} = 7.0 + \frac{1}{2}\text{p}K_a - \frac{1}{2}\text{p}K_b \quad \dots(9.44)$$

We are given:  $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$  and  $K_a(\text{HNO}_2) = 4.5 \times 10^{-4}$ , let's first calculate the corresponding pK values

$$\text{p}K_a = -\log K_a = -\log [4.5 \times 10^{-4}] = -[-3.35] = 3.35$$

$$\text{p}K_b = -\log K_b = -\log [1.8 \times 10^{-5}] = -[-4.74] = 4.74$$

Substituting the values in Eq. (9.44)

$$\text{pH} = 7.0 + \frac{1}{2}(3.35) - \frac{1}{2}(4.74) = 6.31$$

Thus, the pH of the 0.01 M aqueous solution of  $\text{NH}_4\text{NO}_2$  at 298 K would be 6.31.

Recall that in example 9.1 we argued and showed on the basis of degree of hydrolysis that the solution of ammonium nitrite would have an acidic pH. The same is substantiated now on the basis of detailed treatment of the equilibria and we are able even to calculate the pH of the solution.

Having learnt about different aspects of acid-base equilibria of aqueous solutions of different types of salts, solve the following simple questions to assess your understanding.

### SAQ 3

100 cm<sup>3</sup> of 0.02 M sodium hydroxide solution is added to 100 cm<sup>3</sup> of 0.02 M solution of acetic acid at 298 K. Calculate the pH of the resulting solution.

[Given:  $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$ ]

### SAQ 4

Calculate the pH of 0.05 M aqueous solution of ammonium benzoate at 298 K.

[Given:  $K_a(\text{C}_6\text{H}_5\text{COOH}) = 6.5 \times 10^{-5}$ ;  $K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5}$ ]

## 9.4 SOLUBILITY EQUILIBRIA

You know that when we dissolve a solute in a solvent to make solution the amount of solute that dissolves in a given amount of solvent depends on the nature of solute, solvent and the temperature. The amount of solute that dissolves in 100 cm<sup>3</sup> of the solvent at a given temperature is called its **solubility**. Closely related ionic solutes may have widely different solubilities, for example the solubility of NaF is about 4 g at 298 K whereas, we can dissolve about 36 g of sodium chloride in 100 cm<sup>3</sup> of water at same temperature. As against these reasonably soluble ionic solids we can have some solids that are generally referred to as insoluble. For example, in gravimetric determination of chloride ions we precipitate them from their solution as silver chloride for their quantitative determination expecting all the chloride ions to be precipitated on adding silver ion solution.

However, if we take a dried sample of silver chloride, mix it in water and measure its electrical conductivity, we find that the conductivity is far more than that expected of pure distilled water. It indicates that silver chloride does dissolve in water to some extent and dissociates to provide ions that are responsible for the increase in electrical conductivity of its solution. The solubility of silver chloride is found to be about  $1.82 \times 10^{-4}$  g per 100 cm<sup>3</sup> of water at 298 K and such salts with extremely low solubilities are called sparingly soluble salts. We are going to discuss the equilibria in solutions of such sparingly soluble salts.

### 9.4.1 Solubility Product Constant

You have learnt above that when a soluble ionic compound like sodium acetate, dissolves in water, it dissociates completely into hydrated ions. The same holds true for the dissolved sparingly soluble salts also. That is, when a sparingly soluble salt MX is added to water an extremely small fraction of it dissolves and generates ions by dissociation. These ions may combine back to give solid salt and more of the salt may dissolve. Over a period of time equilibrium is established between the ions obtained from the dissociation of dissolved salt and the solid salt i.e., we get a saturated solution of the salt along with the undissolved solid salt. Such equilibrium for a salt of MX type in aqueous solution can be represented as



The corresponding equilibrium constant can be written as

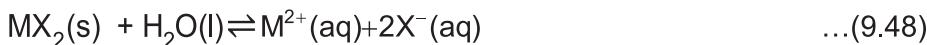
$$K = [\text{M}^+] [\text{X}^-] \quad \dots(9.46)$$

As the equilibrium in Eq. (9.45) is a heterogeneous equilibrium the concentration of solid MX and liquid water would not appear in the expression of equilibrium constant; these are included in the value of K. Thus, the equilibrium constant is essentially the product of the concentrations of the ions obtained from the dissociation of dissolved sparingly soluble salt and is called as **solubility product constant** or simply the **solubility product** and is denoted as  $K_{sp}$ .

$$K_{sp} = [M^+][X^-] \quad \dots(9.47)$$

The magnitude of  $K_{sp}$ , at a given temperature depends on the extent to which the solid solute dissolves to give ions in solution. In other words, it depends on the solubility of salt. We would derive a relationship between the  $K_{sp}$  and the solubility of the sparingly soluble salt a little later. Let's first learn about the expressions for  $K_{sp}$  for different types of salts.

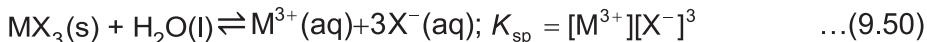
If we dissolve a sparingly soluble salt of say  $MX_2$  type in water the equilibrium can be represented as



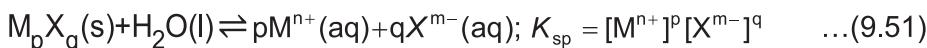
The corresponding expression for  $K_{sp}$  would be

$$K_{sp} = [M^{2+}][X^-]^2 \quad \dots(9.49)$$

As before, the concentration of solid  $MX_2$  and water would not appear in the expression for  $K_{sp}$ . Similarly for salt of  $MX_3$  type dissolved in water the solubility equilibrium and the corresponding expression for  $K_{sp}$  would be



In general for a salt of  $M_pX_q$  type dissolved in water the solubility equilibrium and the corresponding expression for  $K_{sp}$  would be



Thus, the *solubility product constant for a compound is the product of the molar concentrations of the constituent ions in solution, each raised to the power of its stoichiometric coefficient in the solubility equilibrium.*

The values of the solubility product constants of some common sparingly soluble salts at 298 K are given in 9.1.

**Table 9.1: The  $K_{sp}$  values for some common sparingly soluble salts at 298 K**

Salt	$K_{sp}$	Salt	$K_{sp}$
CuS	$6.0 \times 10^{-36}$	AgBr	$5.0 \times 10^{-13}$
Al(OH) <sub>3</sub>	$4.6 \times 10^{-33}$	AgCl	$1.8 \times 10^{-10}$
PbS	$2.5 \times 10^{-27}$	BaSO <sub>4</sub>	$1.1 \times 10^{-10}$
ZnS	$1.1 \times 10^{-21}$	CaCO <sub>3</sub>	$3.8 \times 10^{-9}$
NiS	$3.0 \times 10^{-19}$	PbCl <sub>2</sub>	$1.6 \times 10^{-5}$

Let us learn how to write the solubility equilibrium and expression for  $K_{sp}$  for some sparingly soluble salts in the example 9.5.

**Example 9.5:** Write the solubility equilibrium and expressions for  $K_{sp}$  for the following sparingly soluble salts.



**Solution:** The solubility equilibrium and the expressions for  $K_{sp}$  for the given sparingly soluble salts are as under:

- i. AgCl(s) + H<sub>2</sub>O(l) ⇌ Ag<sup>+</sup>(aq) + Cl<sup>-</sup>(aq);  $K_{sp} = [Ag^+] [Cl^-]$
- ii. MgF<sub>2</sub>(s) + H<sub>2</sub>O(l) ⇌ Mg<sup>2+</sup>(aq) + 2F<sup>-</sup>(aq);  $K_{sp} = [Mg^{2+}] [F^-]^2$
- iii. CaC<sub>2</sub>O<sub>4</sub>(s) + H<sub>2</sub>O(l) ⇌ Ca<sup>2+</sup>(aq) + C<sub>2</sub>O<sub>4</sub><sup>2-</sup>(aq);  $K_{sp} = [Ca^{2+}] [C_2O_4^{2-}]$
- iv. Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(s) + H<sub>2</sub>O(l) ⇌ 2Al<sup>3+</sup>(aq) + 3SO<sub>4</sub><sup>2-</sup>(aq);  $K_{sp} = [Al^{3+}]^2 [SO_4^{2-}]^3$

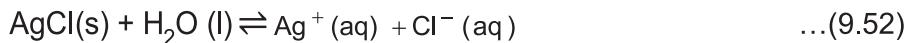
#### 9.4.2 Solubility and Solubility Product Constant

As stated above, the value of  $K_{sp}$  is a measure of the solubility of the sparingly soluble salts; larger the value, the higher the solubility. Let's raise some questions. First, if the  $K_{sp}$  values for two sparingly soluble salts are equal, would their solubility also be equal? And secondly, would the solubility of a salt with higher  $K_{sp}$  value always be greater than that of lower  $K_{sp}$  value?

The answer to these questions is not 'yes' as we cannot compare the solubilities of different salts merely by comparing their  $K_{sp}$  values. It is so because as you would have noticed above, the value of  $K_{sp}$  depends on the solubility of the salt as well as on the formula of the salt. Let us learn about the relationship between the  $K_{sp}$  and the solubility of the sparingly soluble salts of different types.

##### Solubility and $K_{sp}$ for MX Type of Salt

Let us take the dissolution of silver chloride (AgCl) in water as an example of sparingly soluble salt of MX type. The solubility equilibrium would be



The expression for  $K_{sp}$  would be

$$K_{sp} = [Ag^+] [Cl^-]. \quad \dots(9.53)$$

Let's assume that the solubility of AgCl in water at 298 K is 's' mol dm<sup>-3</sup>. This means that if we take a solid sample of silver chloride and try to dissolve it in water then only 's' moles of it would dissolve in 1 dm<sup>3</sup> of distilled water and rest of it would remain as undissolved solid i.e., we would get a saturated solution. The initial and equilibrium concentrations of various ionic species in the solution so obtained would be

Concentration*	$\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})$	
/ mol dm <sup>-3</sup>		
Initial	0	0
Change due to dissociation of AgCl	s	s
At equilibrium	s	s

\* Note that the concentration of the solid AgCl does not change

Thus, the concentration of both the ions at equilibrium would be 's' mol dm<sup>-3</sup> each. Substituting it in the expression for  $K_{\text{sp}}$ , Eq. (9.53) we get

$$K_{\text{sp}} = (s \text{ mol dm}^{-3})(s \text{ mol dm}^{-3}) = s^2 \text{ mol}^2 \text{ dm}^{-6} \quad \dots(9.54)$$

$$\Rightarrow K_{\text{sp}} = s^2 \quad \dots(9.55)$$

Like all equilibrium constants,  $K_{\text{sp}}$  is also dimensionless. However, you must remember that solubility in the expression for  $K_{\text{sp}}$  is in mol dm<sup>-3</sup>. In some cases you may be provided solubilities in terms of g dm<sup>-3</sup> or g per 100 cm<sup>3</sup>, you must convert them into mol dm<sup>-3</sup> so as to calculate the  $K_{\text{sp}}$ . Let's take up an example.

**Example 9.6:** Silver chloride-a sparingly soluble salt has a solubility of  $1.82 \times 10^{-4}$  g per 100 cm<sup>3</sup> at 298 K. Calculate the value of the  $K_{\text{sp}}$  for AgCl at 298 K.

**Solution:** As silver chloride is a MX type of salt, the value of  $K_{\text{sp}}$  would be given by Eq. (9.60) wherein the solubility 's' is in mol dm<sup>-3</sup>. However, we are given the solubility in g per 100 cm<sup>3</sup>. Therefore we would first need to convert it to the units of mol dm<sup>-3</sup>. The approach would be as follows:

Solubility in g per 100 cm<sup>3</sup>  $\rightarrow$  Solubility in g dm<sup>-3</sup>  $\rightarrow$  Solubility in mol dm<sup>-3</sup>  $\rightarrow$  Concentration of Ag<sup>+</sup> and Cl<sup>-</sup> ions in mol dm<sup>-3</sup>  $\rightarrow$   $K_{\text{sp}}$  for AgCl

Given Solubility of AgCl per 100 cm<sup>3</sup> =  $1.82 \times 10^{-4}$  g

$\rightarrow$  Solubility of AgCl in g per dm<sup>3</sup> can be obtained by multiplying the solubility in g per 100 cm<sup>3</sup> by 10 i.e.,

$$= 1.82 \times 10^{-4} \text{ g} \times 10 = 1.82 \times 10^{-3} \text{ g}$$

$\rightarrow$  Solubility in mol dm<sup>-3</sup> can be obtained by dividing solubility in g dm<sup>-3</sup> by the molar mass

$$\Rightarrow s = \frac{1.82 \times 10^{-3}}{M}$$

$$\Rightarrow s = \frac{1.82 \times 10^{-3}}{143.32} = 1.26 \times 10^{-5} \text{ M}$$

Now, as per Eq. (9.55),  $K_{sp} = s^2$

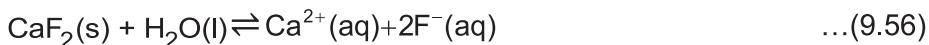
Substituting the value of  $s$  in the Eq. (9.60) we get,

$$K_{sp} = s^2 = (1.26 \times 10^{-5})^2 = 1.58 \times 10^{-10}$$

Thus, the  $K_{sp}$  for AgCl is found to be  $1.58 \times 10^{-10}$

### Solubility and $K_{sp}$ for $MX_2$ Type of Salt

Let us take the dissolution of calcium fluoride ( $CaF_2$ ) in water as an example of sparingly soluble salt of  $MX_2$  type. The solubility equilibrium would be



The expression for  $K_{sp}$  would be

$$K_{sp} = [Ca^{2+}][F^-]^2. \quad \dots(9.57)$$

Let us assume that the solubility of  $CaF_2$  in water at 298 K is ' $s$ ' mol  $dm^{-3}$ . This means that if we take a solid sample of calcium fluoride and try to dissolve it in water then only ' $s$ ' moles of it would dissolve in 1  $dm^3$  of distilled water and rest of it would remain as undissolved solid i.e., we would get a saturated solution. The initial and equilibrium concentrations of various species in solution would be

Concentration / mol $dm^{-3}$	$CaF_2(s) + H_2O(l) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$		
Initial	0	0	
Change due to dissociation	$s$	$2s$	
At equilibrium	$s$	$2s$	

Thus, the concentration of calcium ions at equilibrium would be ' $s$ ' mol  $dm^{-3}$  whereas that of fluoride ions would be twice this amount i.e.,  $2s$  mol  $dm^{-3}$ . Substituting these equilibrium concentrations in the expression for  $K_{sp}$ , Eq. (9.57), we get

$$K_{sp} = (s)(2s)^2 = s \times 4s^2 = 4s^3 \quad \dots(9.58)$$

You may once again note here that we are not using any units for  $K_{sp}$ . In Example 9.6 you have learnt to calculate the value of  $K_{sp}$  by using the solubility of the sparingly soluble salt. You may come across a situation wherein you need to determine the solubility of a sparingly soluble salt by using given value of  $K_{sp}$ . Let's learn the same with the help of another example.

**Example 9.7:** The solubility product for a sparingly soluble salt, calcium fluoride at 298 K is found to be  $4.0 \times 10^{-11}$ . Calculate the solubility of calcium fluoride in g per 100 cm<sup>3</sup> at 298 K.

**Solution:** Calcium fluoride is a MX<sub>2</sub> type of salt and we are provided with the value of  $K_{sp}$  for it and we need to calculate the solubility of calcium fluoride in g per 100 cm<sup>3</sup>. As per Eq. (9.58), the molar solubility and the  $K_{sp}$  for a MX<sub>2</sub> type of salt are related as

$$K_{sp} = 4s^3$$

Determination of solubility is straight forward by rearranging Eq. (9.58) as follows

$$K_{sp} = 4s^3 \rightarrow s = \sqrt[3]{\frac{K_{sp}}{4}} \quad \dots(9.59)$$

This provides solubility in terms of mol dm<sup>-3</sup>; however we need to determine it in g per 100 cm<sup>3</sup>. Therefore, the approach would be as follows:

Calculate the solubility in mol dm<sup>-3</sup> → Solubility in gdm<sup>-3</sup> → Solubility in g per 100 cm<sup>3</sup>. So we begin by determining the solubility in mol dm<sup>-3</sup> by using Eq. (9.59) i.e.,

$$s = \sqrt[3]{\frac{K_{sp}}{4}}$$

Substituting the value of  $K_{sp}$  we get,

$$\begin{aligned} s &= \sqrt[3]{\frac{4.0 \times 10^{-11}}{4}} = \sqrt[3]{1.0 \times 10^{-11}} = (1.0 \times 10^{-11})^{\frac{1}{3}} \\ &= 2.15 \times 10^{-4} \text{ M} \end{aligned}$$

In order to convert the molar solubility to solubility in g dm<sup>-3</sup>, we multiply the molar solubility by molar mass of calcium fluoride i.e.,

$$\text{Solubility in g dm}^{-3} = 2.15 \times 10^{-4} \text{ mol dm}^{-3} \times 78.07 \text{ g mol}^{-1} = 1.68 \times 10^{-2} \text{ g dm}^{-3}$$

The solubility in g per 100 cm<sup>3</sup> would be obtained by dividing solubility in g dm<sup>-3</sup> by 10 i.e.,

$$\text{Solubility in g per 100 cm}^3 = \frac{1.68 \times 10^{-2} \text{ g dm}^{-3}}{10} = 1.68 \times 10^{-3}$$

Thus, the solubility of calcium fluoride would be  $1.68 \times 10^{-3}$  g per 100 cm<sup>3</sup>.

The calculation of cube root can easily be done with the help of log tables as shown below.

$$s = (1.0 \times 10^{-11})^{\frac{1}{3}}$$

Taking logs

$$\begin{aligned} \log s &= \frac{1}{3} \log (1.0 \times 10^{-11}) \\ &= \frac{1}{3}(-11.0) = -3.666 \\ &= 4.3334 \end{aligned}$$

Taking antilog

$$\begin{aligned} s &= \text{antilog}(0.3334) \times 10^{-4} \\ &= 2.15 \times 10^{-4} \end{aligned}$$

As we have worked out the relationship between the solubility and the  $K_{sp}$  for MX and MX<sub>2</sub> types of salts we can derive similar relationships for other types of salts. The relationship between the molar solubility and the  $K_{sp}$  for different types of salts are given in Table 9.2.

**Table 9.2: Relationship between the solubility product constant,  $K_{sp}$  and molar solubility,  $s$  for different types of sparingly soluble salts**

Salt	Salt type	Relationship between $K_{sp}$ and $s$	
AgCl, CaSO <sub>4</sub>	MX	$K_{sp} = s^2$	$s = \sqrt{K_{sp}}$
MgCl <sub>2</sub> , Ag <sub>2</sub> CO <sub>3</sub>	MX <sub>2</sub> , M <sub>2</sub> X	$K_{sp} = 4s^3$	$s = \sqrt[3]{\frac{K_{sp}}{4}}$
Al(OH) <sub>3</sub> ,	MX <sub>3</sub>	$K_{sp} = 27s^4$	$s = \sqrt[4]{\frac{K_{sp}}{27}}$
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> , Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	M <sub>2</sub> X <sub>3</sub> , M <sub>3</sub> X <sub>2</sub>	$K_{sp} = 108 s^5$	$s = \sqrt[5]{\frac{K_{sp}}{108}}$

### SAQ 5

Derive a relationship between the solubility and  $K_{sp}$  for a sparingly soluble salt of M<sub>2</sub>X<sub>3</sub> type having a solubility of  $s$  mol dm<sup>-3</sup>.

## 9.5 EFFECT OF COMMON ION ON SOLUBILITY EQUILIBRIUM

In Unit 8 you have learnt about the effect of common ion on the ionisation equilibrium of weak acids. Let's learn whether the common ions affect the solubility equilibrium also and if yes, what is the effect? Let us attempt to learn it with the help of an example.

**Example 9.8:** Calculate the molar solubility of CaF<sub>2</sub> - a sparingly soluble salt in 0.01 M solution of NaF at 298 K and compare the result with the one obtained in example 9.7.[Given:  $K_{sp}(\text{CaF}_2) = 4.0 \times 10^{-11}$  at 298K]

**Solution:** In example 9.7 we calculated the solubility of calcium fluoride in water to be:  $2.15 \times 10^{-4}$  M. Let us calculate the same in 0.01 M solution of NaF here.

In order to calculate the solubility in a solution of 0.01 M NaF we assume that the solubility of CaF<sub>2</sub> in this solution is  $s$  mol dm<sup>-3</sup>. The initial and equilibrium concentrations of various species in the solution would be as follows:

Concentration/ mol dm <sup>-3</sup>	CaF <sub>2</sub> (s) + H <sub>2</sub> O(l)	$\rightleftharpoons$	Ca <sup>2+</sup> (aq)	-	2F <sup>-</sup> (aq)
Initial			0		0
Change due to dissociation of CaF <sub>2</sub>			$s$		$2s$
Change due to dissociation of 0.01 M NaF (a strong electrolyte)			--		0.01
At equilibrium			$s$		$2s + 0.01$

The expression for  $K_{sp}$  of  $\text{CaF}_2$  is:  $K_{sp} = [\text{Ca}^{2+}] [\text{F}^-]^2$

Substituting the values of  $K_{sp}$  and the equilibrium concentrations from the table in the expression for  $K_{sp}$  we get

$$4.0 \times 10^{-11} = [s][2s + 0.01]^2$$

Assuming that the solubility is very low we ignore  $2s$  in comparison to  $0.01 \text{ M}$  and write

$$4.0 \times 10^{-11} = [s][0.01]^2 \Rightarrow s = 4.0 \times 10^{-7} \text{ mol dm}^{-3}$$

As the value of solubility obtained is far less than  $0.01$  our assumption is valid. Further, we observe that the solubility of the sparingly soluble salt  $\text{CaF}_2$  has decreased from  $2.15 \times 10^{-4} \text{ M}$  (in water) to about  $4.0 \times 10^{-7} \text{ M}$  in presence of  $0.01 \text{ M}$  sodium fluoride—an electrolyte containing common ion. Thus, the solubility would decrease by about 535 times.

On the basis of example 9.8 we can say that the common ions do affect the solubility equilibria in the same way as any other equilibrium. You may also note that the value of  $K_{sp}$  depends only on the temperature, and not on the individual ion concentrations. As we have seen in the example, addition of a salt having common ions shifted the equilibrium to the left however, the value of  $K_{sp}$  was maintained.

### **$K_{sp}$ and Precipitation**

We have defined solubility product constant as the product of the concentration of the ions obtained from the dissociation of dissolved sparingly soluble salt. These concentrations are raised to the power equal to their stoichiometric coefficient in the equilibrium expression. It depends on the solubility of the salt and its value is indicative of the same. If we try to think of the solubility equilibrium slightly differently, we find that it also gives an idea about the product of the concentration of ions that can remain in solution. Which means that if the product of the concentration of ions were more than  $K_{sp}$  the ions would combine and form solid or in other words they would form a **precipitate**.

It is worthwhile to recall here the concept of reaction quotient,  $Q$  about which you have learnt in subsection 6.2.3. You would recall that reaction quotient has the same mathematical form as the equilibrium constant expression but uses actual concentrations of different species in the mixture, instead of equilibrium concentrations used in equilibrium constant. In the context of solubility equilibrium we can define an equivalent of reaction quotient as ion-product (or ionic-product),  $Q_{sp}$ . For example, the expressions for  $K_{sp}$  and  $Q_{sp}$  for lead chloride would be

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2; Q_{sp} = [\text{Pb}^{2+}]_i[\text{Cl}^-]_i^2 \quad \dots(9.60)$$

We have to keep in mind that in case of  $K_{sp}$  we use equilibrium concentrations and for  $Q_{sp}$  the concentrations at any instant (generally initial or at the time of

mixing) are used. In order to determine whether ions in a solution will form a precipitate or not we need to compare the values of  $K_{sp}$  and  $Q_{sp}$ . If,

$Q_{sp} > K_{sp}$ ; there would be precipitation

$Q_{sp} < K_{sp}$ ; there would not be any precipitation

$Q_{sp} = K_{sp}$ ; we would get a saturated solution; still no precipitation

Let's us take an example.

**Example 9.9:** Will a precipitate of  $PbI_2$  be formed if we add 2 drops of 0.1 M KI solution to  $10\text{ cm}^3$  of a solution containing  $0.01\text{M}$   $Pb^{2+}$  ions at  $298\text{ K}$ ? Assume that the drop volume is  $0.05\text{ cm}^3$  and there is no dilution of lead ion solution on adding KI.  
[Given:  $K_{sp}(PbI_2) = 7.0 \times 10^{-9}$  at  $298\text{K}$ ]

**Solution:** The approach to solve this problem is very straightforward. We need to calculate the concentration of the added iodide ion and compute the value of  $Q_{sp}$  for  $PbI_2$  and compare it with the given value of  $K_{sp}$ .

The volume of KI added  $= V_1 = 0.05 \times 2 = 0.1\text{ cm}^3$

Concentration of KI  $= M_1 = 0.1\text{ M}$

Final volume  $= V_2 = 10.1\text{ cm}^3$

$$\Rightarrow \text{Concentration of } I^- \text{ ions} = \frac{M_1 \times V_1}{V_2} = \frac{0.1 \times 0.1}{10.1} = 1.0 \times 10^{-3}\text{ M}$$

As there is no dilution of lead ion solution  $\Rightarrow [Pb^{2+}] = 0.01\text{ M}$

$$\Rightarrow Q_{sp} = [Pb^{2+}] [I^-]^2 = (0.01) \times (0.001)^2 = 1.0 \times 10^{-8}$$

As the value of  $Q_{sp}(1.0 \times 10^{-8})$  is more than  $K_{sp}(7.0 \times 10^{-9})$  for  $PbI_2$  there will be precipitation of lead iodide from the solution.

*Would the precipitate of  $PbI_2$  be formed if we use just 1 drop of KI in place of two drops? (Answer: No; Check by calculation.)*

### pH and Solubility

Let's raise a question, "Does the solubility of a sparingly soluble salt depend on the pH of the medium?" To answer this we take two examples, first let's consider the dissolution of magnesium hydroxide,  $Mg(OH)_2$  –a sparingly soluble metal hydroxide commonly used as an antacid.



In acidic medium, say in stomach, the hydroxide ions obtained from the dissociation of magnesium hydroxide would combine with the hydronium ions in the stomach to give water molecules.



As the hydroxyl ions get consumed in the process then according to the Le-Chatelier principle the solubility equilibrium Eq. (9.61) for magnesium hydroxide, would shift to right. This implies that more of  $Mg(OH)_2$  would dissolve to maintain the equilibrium constant i.e., the solubility will increase.

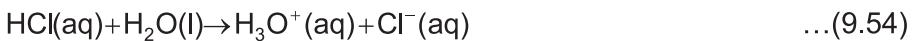
Let's take another example, say of solubility of  $CaF_2$  in a solution of hydrochloric acid.  $CaF_2$  is a salt of a weak acid HF; the solubility equilibrium in its aqueous solution would be as under.



The fluoride ions – conjugate base of weak acid (HF) are expected to get hydrolysed in solution as given below



The added hydrochloric acid (a strong acid), on the other hand would ionise completely to provide hydronium ions.



The hydronium ions so produced neutralise the hydroxyl ions obtained from hydrolysis. As a consequence the hydrolysis equilibrium of fluoride ions shifts to the right i.e., more fluoride ions are hydrolysed. As the fluoride ions are removed from the equilibrium mixture, more  $CaF_2$  dissolves to maintain the equilibrium. Thus, we see that the solubility of calcium fluoride increases in an acidic solution.

Similarly we can show that in case of a salt of a weak base and strong acid, the cation of the salt would get hydrolysed to give hydronium ions. In such a case the solubility would increase in basic medium because the added hydroxyl ions would neutralize the hydronium ions obtained from the hydrolysis of the cation and shift the equilibrium to the right.

The solubilities of metal hydroxides and salts of weak acids / bases depend on the concentration of hydronium/ hydroxyl ions or the pH of the solution. In such cases the hydronium / hydroxyl ions are not a part of the equilibrium but they alter the equilibrium by consuming or eliminating one of the species from the equilibrium. This in turn affects the solubility equilibrium and hence the solubility.

## 9.6 APPLICATIONS OF SOLUBILITY PRODUCT PRINCIPLE

The solubility product constant and the effect of common ions and pH on solubility equilibrium find a wide variety of applications in industry and analytical determination. Some of the common applications of the solubility product principle are as under.

- Salting out of soap
- Purification of sodium chloride

- Qualitative determinations in the laboratory
- Quantitative determinations in the laboratory

Let us discuss these one by one.

### **Salting out of soap**

As you know that soaps are generally sodium or potassium salts of higher fatty acids like stearic acid. These are prepared by alkaline hydrolysis (or saponification) of fats and oils, or their fatty acids. In this process, the oil or fat is heated with a concentrated solution of alkali (e.g., NaOH). The higher fatty acids obtained by the hydrolysis of oil or fat are neutralised by alkali to form the soap. Part of the soap precipitates out but a large amount of it stays dissolved in the reaction mixture. For example, the solution equilibrium for sodium stearate is as under



In order to recover soap from the solution we exploit the effect of common ion on the equilibrium and add a concentrated solution of sodium chloride (or sometimes crystals of NaCl). This increases the concentration of sodium ions in the reaction mixture and separate the soap out of solution by shifting the equilibrium given in Eq. (9.64) to the left. As the soap comes out of the solution by added salt this process is called as **salting out of soap**.

### **Purification of sodium chloride**

Sodium chloride (common salt) is generally obtained from natural source (sea water) and is contaminated with salts of other metals and other impurities. This needs to be purified before being used. One of the methods of purification of sodium chloride exploits the effect of common ion on the solubility equilibrium. For this purpose a saturated solution of the impure sodium chloride is prepared and filtered to remove impurities. Thereafter a stream of hydrogen chloride gas is passed through the solution. The HCl gas in water is solvated and gets fully ionised to hydronium and chloride ions. As this provides a large concentration of chloride ions the ionic product of sodium and chloride ions ( $Q_{\text{NaCl}}$ ) exceed the solubility product ( $K_{\text{SP}}$ ) of NaCl; thereby pure crystalline salt is obtained. Other salts stay in solution.

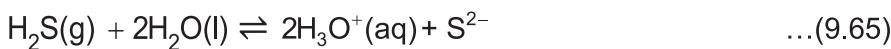
### **Qualitative determinations in the laboratory**

You would have learnt and performed qualitative salt analysis in your earlier classes wherein one identifies the cation (s) and anion (s) in the given salt (or a salt mixture). You would recall that in cation analysis the cations are placed in six different groups (I to VI) and we use a specific reagent to check for the presence of cations of a given group. The cations of a given group are then identified by the colour and nature of the precipitate formed. The grouping of cations in this scheme is based on the principles of solubility product, its relationship with the solubility and the effect of common ions and pH on the solubility equilibrium. Let's learn about the separation of the groups in cation analysis.

You would recall that the group reagent for the first group happens to be dil. HCl. This provides chloride ions that precipitate the group I cations as their chlorides.

When we add dil. HCl to the salt solution containing different cations, the  $\text{Pb}^{2+}$ ,  $\text{Hg}_2^{2+}$  and  $\text{Ag}^+$  are precipitated because their chlorides are sparingly soluble and their solubility product is exceeded whereas all other chlorides with higher solubility product stay in solution. The precipitated chlorides are removed by filtration and identified.

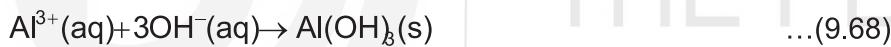
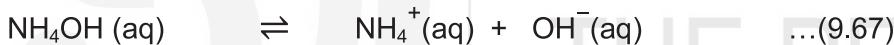
The group II cations are precipitated as sulphides. The group reagent for second group is  $\text{H}_2\text{S}$  gas that is passed into the acidic solution obtained as a filtrate after removing the precipitates of the first group cations.  $\text{H}_2\text{S}$  ionises in aqueous solution to provide sulphide ions that precipitate the cations.



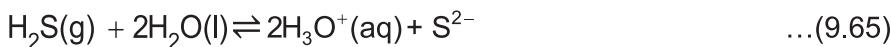
The hydronium ions (from ionisation of HCl) act as a common ion and suppress the ionisation of  $\text{H}_2\text{S}$ , which is a weak diprotic acid. The concentration of sulphides ions becomes very low and as a consequence only those cations are precipitated whose sulphides have low solubility product. For example, CuS with a  $K_{\text{sp}} = 6.0 \times 10^{-37}$  is precipitated whereas NiS with a  $K_{\text{sp}} = 1.4 \times 10^{-24}$  stays in solution.

Sometimes, Lead cation can appear in Group II as well because  $\text{PbCl}_2$  is somewhat soluble (it has moderate solubility product) and therefore it may not be completely precipitated by HCl.

In the third group the ammonium chloride followed by ammonia (or ammonium hydroxide) is used as the group reagent, which is added to the filtrate of second group after boiling off the  $\text{H}_2\text{S}$ . Ammonium hydroxide ionises to provide hydroxide ions that precipitate the cations as hydroxides. These are filtered and analysed.



Here the added ammonium chloride provide ammonium ions that suppress the ionisation of ammonium hydroxide (ammonia in water) thereby decreasing the concentration of hydroxyl ions. As a consequence only the hydroxides of the third group cations having low value of the  $K_{\text{sp}}$  get precipitated. For the fourth group we pass  $\text{H}_2\text{S}$  again but the medium is alkaline due to the added ammonia in the third group.



In this medium, the hydroxide ions from ammonium hydroxide react with the hydronium ions obtained from the ionisation of  $\text{H}_2\text{S}$  to produce water and shift the ionisation equilibrium of  $\text{H}_2\text{S}$  in the forward direction thereby increasing the concentration of sulphides ions. As a consequence the cations whose sulphides have high solubility product are also precipitated. Remember that these were not precipitated in the acidic medium of group II.



In the fifth group the reagent is ammonium carbonate and the cations are precipitated as their carbonates. The precipitates are filtered and identified. Once the carbonates are precipitated and filtered the filtrate may contain  $\text{Na}^+$ ,  $\text{K}^+$  or

$\text{NH}_4^+$  ions. All the salts of these cations are soluble so these are identified with specific tests.

### Quantitative determinations in the laboratory

One of the important methods of quantitative determination in the Chemistry laboratory is gravimetric analysis. In this method the ion to be determined is reacted with a suitable reagent so as to quantitatively convert it into a precipitate. This precipitate is then filtered, dried and weighed. The mass of the precipitate so obtained is proportional to the amount of ion being determined. In these determinations, the concepts of solubility product and the factors affecting it are very crucial. Suitable methods could be devised for selective precipitation and determination of an ion from a mixture purely on the basis of solubility product. For example, if we have a mixture of 0.01 M  $\text{Ag}^+$  and 0.01 M  $\text{Pb}^{2+}$  ions in a solution we can selectively precipitate silver ions by controlling the concentration of precipitating chloride ions. The  $K_{\text{sp}}$  values for  $\text{AgCl}$  and  $\text{PbCl}_2$  are  $1.8 \times 10^{-10}$  and  $1.7 \times 10^{-5}$  respectively. Let us calculate the concentration of chloride ions required to precipitate  $\text{AgCl}$  and  $\text{PbCl}_2$  respectively.

The  $K_{\text{sp}}$  for silver chloride,  $K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$

Concentration of  $\text{Ag}^+$  ions in solution = 0.01 M

Concentration of chloride ions required for precipitation of silver chloride can be calculated by using the fact that the precipitation occurs when ionic product constant ( $Q_{\text{sp}}$ ) is greater than the solubility product constant, i.e.,

$$Q_{\text{sp}} > K_{\text{sp}};$$

$$[\text{Ag}^+][\text{Cl}^-] > K_{\text{sp}} \Rightarrow [\text{Cl}^-] > \frac{K_{\text{sp}}}{[\text{Ag}^+]}$$

Substituting the values,

$$[\text{Cl}^-] > \frac{1.8 \times 10^{-10}}{0.01} = 1.8 \times 10^{-8} \text{ M}$$

Thus, silver chloride would precipitate when the concentration of chloride ions is more than  $1.8 \times 10^{-8}$  M. Similarly, we calculate the concentrations of chloride ions required for precipitating lead chloride

The  $K_{\text{sp}}$  for lead chloride,  $K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$

Concentration of  $\text{Pb}^{2+}$  ions = 0.01 M

Concentration of chloride ions required for precipitation of lead chloride =

$$[\text{Cl}^-]^2 > \frac{K_{\text{sp}}}{[\text{Pb}^{2+}]} = \frac{1.7 \times 10^{-5}}{0.01} = 1.7 \times 10^{-3}$$

Substituting the values,

$$[\text{Cl}^-] > \sqrt{1.7 \times 10^{-3} \text{ M}} = 4.12 \times 10^{-2} \text{ M}$$

So you can see that we need a little more than  $1.8 \times 10^{-8}$  M chloride ions for the precipitation of AgCl to take place whereas for PbCl<sub>2</sub> to be precipitated we need at least  $4.12 \times 10^{-2}$  M chloride ions. Thus, by suitably controlling the concentration of chloride ions we can selectively precipitate silver ions whereas the lead ions would stay in solution.

### SAQ 6

An aqueous solution contains Ba<sup>2+</sup> and Sr<sup>2+</sup> ions at a concentration of  $10^{-5}$  M and  $10^{-1}$  M respectively. Which of the ions would precipitate first on adding a solution of potassium chromate dropwise to the mixture? Assume that there is no dilution.

[Given:  $K_{sp}(\text{BaCrO}_4) = 1.2 \times 10^{-10}$ ;  $K_{sp}(\text{SrCrO}_4) = 3.5 \times 10^{-5}$  at 298K]

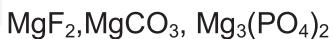
## 9.7 SUMMARY

In this last unit of the block on Chemical and Ionic Equilibrium we continued our discussion on ionic equilibrium and focused on the hydrolysis of salts in aqueous solutions and the solubility of sparingly soluble salts. In a typical process of dissolution of a salt in water the water molecules hydrate the ions of the salt and as a result of the energy released in the process the ions dissociate from the lattice and are released in the solution. Thereafter, the anions of weak acids and cations of weak bases react with water and get hydrolysed. The hydrolysis of anions of weak acids involves accepting a hydrogenion from water and generating hydroxide ions in solution thus making the solution alkaline. On the other hand, the hydrolysis of cations of weak bases involves donating a hydrogen ion to water and generating hydronium ions in solution thus making the solution acidic. In case of salts of weak acids and weak bases both the ions get hydrolysed and the nature of solution is determined by the ions getting hydrolysed to a greater extent. The ions obtained on dissolution of a salt of a strong acid and a strong base, do not get hydrolysed and their solution is neutral. The hydrolysis equilibrium of an ion is characterised in terms of a hydrolysis constant that is related to the  $K_a$  or  $K_b$  of the conjugate acid or base of the ion getting hydrolysed and the ionic product of water.

When a sparingly soluble salt is added to water an extremely tiny fraction of it gets dissolved and like any other salt it dissociates into ions that get hydrated. However, most of the salt remains undissolved and equilibrium exists between the solid salt and the ions. This heterogeneous equilibrium is recognised in terms of equilibrium constant called as solubility product constant,  $K_{sp}$ . The solubility product of a salt is related to its molar solubility and the relationship depends on the formula of the salt. Further, like any other equilibrium the solubility equilibrium is also affected by the presence of common ions. The solubility equilibrium is suppressed by the presence of common ions and the solubility decreases. In addition to the common ions the pH of the solution also affects the solubility in cases of metal hydroxides and the salts of weak acids and bases. The solubility product and the effect of common ions and pH on solubility equilibrium find a wide variety of applications in industry and analytical determination strategies. Some of the common applications like, salting out of soap, purification of sodium chloride and qualitative & quantitative determinations in the laboratory have also been discussed.

## 9.8 TERMINAL QUESTIONS

- Give the equilibrium representing hydrolysis of an anion of a weak acid in aqueous solution and derive a relationship between the hydrolysis constant of the anion and acid dissociation constant of the weak acid.
- Define degree of hydrolysis. Write down the equilibrium reaction for the hydrolysis of anion in a salt NaA of a weak acid, HA, and calculate the pH of its 0.10 M solution. [Given:  $K_a(\text{HA}) = 1.8 \times 10^{-4}$  at 298K].
- Sodium benzoate is used as a food preservative. Calculate the pH of 0.01 M aqueous solution of sodium benzoate at 298 K. [Given:  $K_a(\text{benzoic acid}) = 6.5 \times 10^{-5}$  at 298K].
- Write the solubility product expressions for the following salts:
  - $\text{PbCl}_2$
  - $\text{Ag}_2\text{S}$
  - $\text{Al}(\text{OH})_3$
  - $\text{NiS}$
  - $\text{BaCO}_3$
- Calcium oxalate—one of the significant constituents of kidney stones has a solubility of  $6.1 \times 10^{-3}$  g dm<sup>-3</sup>. Calculate the value for  $K_{sp}$  for calcium oxalate.
- Derive a relationship between the  $K_{sp}$  and molar solubility of ammonium carbonate.
- Calculate the molar solubility of  $\text{CaF}_2$  - a sparingly soluble salt in 0.01 M calcium nitrate solution at 298 K. Compare the result with that obtained in example 9.8. [Given:  $K_{sp}(\text{CaF}_2) = 4.0 \times 10^{-11}$  at 298K]. What inference do you draw?
- Arrange the following salts of magnesium in the order of increasing solubilities.



[Given:  $K_{sp}(\text{MgF}_2) = 3.7 \times 10^{-8}$ ,  $K_{sp}(\text{MgCO}_3) = 3.5 \times 10^{-8}$ ,  $K_{sp}(\text{Mg}_3(\text{PO}_4)_2) = 1.0 \times 10^{-25}$  at 298K].

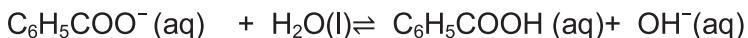
## 9.9 ANSWERS

### Self-Assessment Questions

- Salt hydrolysis refers to the reaction of the ion (s) of the salt with water. The dissolution of sodium benzoate in water involves hydration of the ions followed by their dissociation from the lattice. The overall process can be given as



Of these, the sodium ions do not react with water whereas benzoate ions would get hydrolysed and the hydrolysis equilibrium can be given as



The degree of hydrolysis for an anion of a weak acid is given by the following expression, Eq. (9.23)

$$\alpha = \sqrt{\frac{K_w}{K_a c}}$$

where  $K_a$  is the acid dissociation constant for the conjugate acid  $C_6H_5COOH$ , here. Substituting the values of  $K_w$ ,  $K_a$ , and  $c$  at 298 K we get

$$\Rightarrow \alpha = \sqrt{\frac{1.0 \times 10^{-14}}{6.5 \times 10^{-5} \times 10^{-2}}} = \sqrt{1.54 \times 10^{-8}} = 1.24 \times 10^{-4}$$

The degree of hydrolysis of benzoate ions in 0.01 M aqueous solution of sodium benzoate is found to be  $= 1.24 \times 10^{-4}$

2. The details of the ions that will be hydrolysed in the given salts and the acid-base nature of the resulting solutions are as under

Salt	Ion (s) getting hydrolysed	Acid-base nature of the aqueous solution of salt
HCOONa	$HCOO^-$	Basic
$NH_4Br$	$NH_4^+$	Acidic
$C_6H_5COONH_4$	$C_6H_5COO^-$ and $NH_4^+$	Acidic*

\* The degree of hydrolysis is inversely proportional to the square root of the acid/ base dissociation constant of the conjugate acid/ base of the ion getting hydrolysed. As the dissociation constant of ammonium hydroxide is less than that of benzoic acid, ammonium ions would hydrolyse more than benzoate ion. As a consequence the solution would be acidic.

3. To begin with we are dealing with a simple neutralisation reaction between a strong base and a weak acid to generate a salt and water. The reaction can be given as



We need to first calculate the amounts of reactants in the solution.

$$\text{Amount of NaOH} = \frac{0.02 \text{ moles}}{1000 \text{ cm}^3} \times 100 \text{ cm}^3 = 0.002 \text{ moles}$$

$$\text{Amount of } CH_3COOH = \frac{0.02 \text{ moles}}{1000 \text{ cm}^3} \times 100 \text{ cm}^3 = 0.002 \text{ moles}$$

Thus, 2 millimoles of NaOH are reacting with 2 millimoles of acetic acid. As the acid and base are in equal amounts their neutralisation will generate 2 millimoles of salt (sodium acetate). However this salt will be present in a total volume of 200 cm<sup>3</sup>. Thus,

- Molar concentration of sodium acetate in solution

$$= \frac{0.002 \text{ moles}}{200 \text{ cm}^3} \times 1000 \text{ cm}^3 = 0.01 \text{ M}$$

As sodium acetate is a salt of weak acid and strong base its anion would get hydrolysed. The pH of such a solution is given by the following expression, Eq. (9.36).

$$\Rightarrow \text{pH} = 7.0 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log c \quad \dots(9.36)$$

Let's first calculate the  $\text{p}K_a$  for acetic acid (the conjugate acid of the anion)

$$\text{p}K_a = -\log K_a = -\log[1.8 \times 10^{-5}] = -[-4.74] = 4.74$$

Substituting the values at 298 K in Eq. (9.36).

$$\begin{aligned} \text{pH} &= 7.0 + \frac{1}{2}(4.74) + \frac{1}{2} \log(0.01) \\ \Rightarrow \text{pH} &= 7.0 + 2.37 + \frac{1}{2}(-2.0) = 9.37 - 1.0 = 8.37 \end{aligned}$$

The pH of the resulting solution would be 8.37

4. Ammonium benzoate is a salt of a weak acid and a weak base. The pH of aqueous solution of such a salt is given by Eq. (9.44).

$$\text{pH} = 7.0 + \frac{1}{2} \text{p}K_a - \frac{1}{2} \text{p}K_b \quad \dots(9.44)$$

We are given:

$$K_b(\text{NH}_4\text{OH}) = 1.8 \times 10^{-5} \text{ and } K_a(\text{C}_6\text{H}_5\text{COOH}) = 6.5 \times 10^{-5}$$

Let's first calculate the corresponding  $\text{p}K$  values

$$\text{p}K_a = -\log K_a = -\log[6.5 \times 10^{-5}] = -[-4.19] = 4.19$$

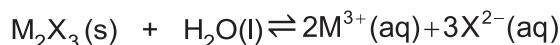
$$\text{p}K_b = -\log K_b = -\log[1.8 \times 10^{-5}] = -[-4.74] = 4.74$$

Substituting the values in Eq. (9.44),

$$\text{pH} = 7.0 + \frac{1}{2}(4.19) - \frac{1}{2}(4.74) = 6.73$$

Thus, the pH of the given solution of sodium benzoate would be 6.73

5. For the dissolution of a salt of  $M_2X_3$  type the equilibrium would be



The expression for  $K_{sp}$  would be  $K_{sp} = [M^{3+}]^2[X^{2-}]^3$ .

If we assume that the solubility of the salt in water at 298 K is 's' mol  $\text{dm}^{-3}$ , the initial and equilibrium concentrations of various species in the solution would be

Concentration/ mol $\text{dm}^{-3}$	$M_2X_3(s) + H_2O(l) \rightleftharpoons 2M^{3+}(aq) + 3X^{2-}(aq)$		
Initial		0	0
Change due to ionisation		$2s$	$3s$
At equilibrium		$2s$	$3s$

Substituting the equilibrium concentrations in the expression for  $K_{sp}$ , we get

$$K_{sp} = (2s)^2(3s)^3 = 4s^2 \times 27s^3 = 108s^5$$

$$\Rightarrow K_{sp} = 108s^5$$

6. In order to decide the ion precipitating first we need to compute the concentration of potassium chromate required for their respective precipitation and the one requiring lesser amount would precipitate first. Let's calculate the concentrations of precipitating agent required.

The  $K_{sp}$  for barium chromate =  $K_{sp} = [\text{Ba}^{2+}][\text{CrO}_4^{2-}]$

Concentration of  $\text{Ba}^{2+}$  ions =  $10^{-6}$  M

Concentration of chromate ions required for precipitation of barium chromate can be calculated by using the fact that the precipitation occurs when ionic-product is greater than the solubility product, i.e.,

$$Q_{sp} > K_{sp}$$

$$[\text{Ba}^{2+}][\text{CrO}_4^{2-}] > K_{sp}$$

$$[\text{CrO}_4^{2-}] > \frac{K_{sp}}{[\text{Ba}^{2+}]}$$

Substituting the values,

$$[\text{CrO}_4^{2-}] > \frac{1.2 \times 10^{-10}}{10^{-6}} = 1.2 \times 10^{-4} \text{ M}$$

Thus, barium chromate would precipitate when the concentration of chromate ions is more than  $1.2 \times 10^{-4}$  M. Similarly, we calculate the concentrations of precipitating agent required for precipitating strontium chromate

The  $K_{sp}$  for strontium chromate =  $K_{sp} = [\text{Sr}^{2+}][\text{CrO}_4^{2-}]$

Concentration of  $\text{Sr}^{2+}$  ions =  $10^{-1}$  M

Concentration of chromate ions required for precipitation of strontium chromate =

$$[\text{CrO}_4^{2-}] > \frac{K_{sp}}{[\text{Sr}^{2+}]} = \frac{3.5 \times 10^{-5}}{10^{-1}} = 3.5 \times 10^{-4} \text{ M}$$

As the concentration of chromate ions required for the precipitation of barium ions is low they will be precipitating first.

## **Terminal Questions**

1. Let us take HA as the weak acid. Its anion,  $A^-$  would react with water and get hydrolysed. The equilibrium representing hydrolysis of the anion can be represented as:



The expression for hydrolysis constant would be

$$K_h = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

Multiplying the numerator and denominator of the hydrolysis constant expression by concentration of hydronium ions,  $[\text{H}_3\text{O}^+]$  and reorganising the terms we get,

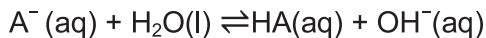
$$K_h = \frac{[\text{HA}][\text{OH}^-][\text{H}_3\text{O}^+]}{[\text{A}^-][\text{H}_3\text{O}^+]}$$

$$K_h = \frac{[\text{HA}]}{[\text{A}^-][\text{H}_3\text{O}^+]} \times [\text{OH}^-][\text{H}_3\text{O}^+]$$

$$\Rightarrow K_h = \frac{1}{K_a} \times K_w$$

The relation suggests that the hydrolysis constant of an anion of a weak acid is inversely related to the acid dissociation constant of the weak acid.

2. Degree of hydrolysis may be defined as the fraction of the total ions of a given type that react with water and get hydrolysed. The general reaction for the hydrolysis of anion of the salt NaA, i.e.,  $\text{A}^-$  can be shown as under



The pH of an aqueous solution of an anion of a weak acid is given in terms of Eq. (9.36)

$$\text{pH} = 7.0 + \frac{1}{2}\text{p}K_a + \frac{1}{2}\log c$$

We are given the value of  $K_a$  for the weak acid, which can be used to calculate the  $\text{p}K_a$  value for HA

$$\text{p}K_a = -\log K_a = -\log[1.8 \times 10^{-4}] = -[-3.74] = 3.74$$

Substituting the values of  $K_a$  and  $c$  in Eq. (9.36)

$$\Rightarrow \text{pH} = 7.0 + \frac{1}{2}(3.74) + \frac{1}{2}\log(1.0 \times 10^{-1})$$

$$\Rightarrow \text{pH} = 7.0 + 1.87 + \frac{1}{2}(-1.00) = 8.87 - 0.50 = 8.37$$

Thus, the pH of the solution would be 8.37.

3. Sodium benzoate is a salt of weak acid (benzoic acid) and a strong base (sodium hydroxide). On dissolution in water, the anion of the salt i.e., benzoate ion would get hydrolysed. The hydrolysis equilibrium can be given as



The pH of the solution can be calculated by using Eq. (9.36)

$$\text{pH} = 7.0 + \frac{1}{2} \text{p}K_a + \frac{1}{2} \log c$$

We are given the value of  $K_a$  for the benzoic acid, which can be used to calculate the  $\text{p}K_a$  value

$$\text{p}K_a = -\log K_a = -\log [6.51 \times 10^{-5}] = -[-4.18] = 4.18$$

Substituting the values of  $K_a$  and  $c$  in Eq. (9.36)

$$\Rightarrow \text{pH} = 7.0 + \frac{1}{2}(4.18) + \frac{1}{2} \log(1.0 \times 10^{-2})$$

$$\Rightarrow \text{pH} = 7.0 + 2.09 + \frac{1}{2}(-2.00) = 9.09 - 1.00 = 8.09$$

The pH of 0.01 M solution of sodium benzoate would be = 8.09

4. The solubility product expressions for the given sparingly soluble salts are as under

i)  $\text{PbCl}_2$ :  $K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$

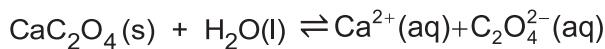
ii)  $\text{Ag}_2\text{S}$ :  $K_{sp} = [\text{Ag}^+]^2[\text{S}^{2-}]$

iii)  $\text{Al(OH)}_3$ :  $K_{sp} = [\text{Al}^{3+}][\text{OH}^-]^3$

iv)  $\text{NiS}$ :  $K_{sp} = [\text{Ni}^{2+}][\text{S}^{2-}]$

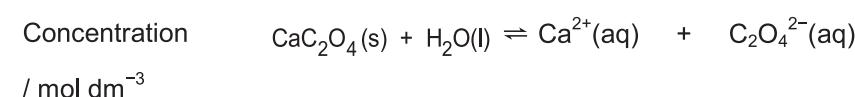
v)  $\text{BaCO}_3$ :  $K_{sp} = [\text{Ba}^{2+}][\text{CO}_3^{2-}]$

5. The solubility equilibrium for calcium oxalate can be given as



The expression for  $K_{sp}$  would be  $K_{sp} = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]$

If we assume that the solubility of  $\text{CaC}_2\text{O}_4$  in water at 298 K is  $s$  mol  $\text{dm}^{-3}$  then initial and equilibrium concentrations of various ionic species in the solution would be



Initial	0	0
Change due to ionisation	$s$	$s$
At equilibrium	$s$	$s$

Substituting the equilibrium concentrations in the expression for  $K_{sp}$ , we get

$$K_{sp} = (s)(s) = s^2$$

Where solubility is in mol dm<sup>-3</sup>, however we are given solubility in g dm<sup>-3</sup>. To convert it to mol dm<sup>-3</sup> we need to divide the given solubility by the molar mass of calcium oxalate (128.1 g mol<sup>-1</sup>)

→ Solubility in mol dm<sup>-3</sup>=

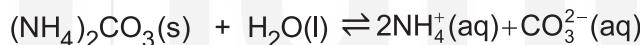
$$\frac{\text{Solubility in gdm}^{-3}}{\text{Molar mass}} = \frac{6.1 \times 10^{-3}}{128.1} = 4.76 \times 10^{-5} \text{ M}$$

Substituting in the expression for  $K_{sp}$ , we get

$$K_{sp} = s^2 = (4.76 \times 10^{-5})^2 = 2.27 \times 10^{-9}$$

The value of  $K_{sp}$  for calcium oxalate is found to be =  $2.27 \times 10^{-9}$

6. The equilibrium reaction for the dissolution of ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3$ ) can be given as



The expression for  $K_{sp}$  would be =  $K_{sp} = [\text{NH}_4^+]^2[\text{CO}_3^{2-}]$

If we assume that the solubility of  $(\text{NH}_4)_2\text{CO}_3$  in water at 298 K to be  $s$  mol dm<sup>-3</sup> then the initial and equilibrium concentrations of various ionic species in solution would be

Concentrations (mol dm <sup>-3</sup> )	$(\text{NH}_4)_2\text{CO}_3(s) + \text{H}_2\text{O}(l) \rightleftharpoons 2\text{NH}_4^+(aq) + \text{CO}_3^{2-}(aq)$	Initial	0	0
Change due to ionisation			2s	s
At equilibrium			2s	s

Substituting the equilibrium concentrations from the table in the expression for  $K_{sp}$ , we get

$$K_{sp} = (2s)^2(s) = 4s^2 \times s = 4s^3$$

This is the desired relationship between the  $K_{sp}$  and the molar solubility of ammonium carbonate.

7. In order to calculate the solubility in of  $\text{CaF}_2$  in 0.01 M calcium nitrate we assume that the solubility of  $\text{CaF}_2$  in 0.01 M calcium nitrate is  $s$  mol dm<sup>-3</sup>. The initial and equilibrium concentrations of various ionic species in solution would be as follows:

Concentration / mol dm <sup>-3</sup>	CaF <sub>2</sub> (s) + H <sub>2</sub> O(l) ⇌ Ca <sup>2+</sup> (aq) + 2F <sup>-</sup> (aq)	
Initial	0	0
Change due to dissociation	s	2s
Change due to dissociation of 0.01 M Calcium nitrate (a strong electrolyte)	0.01	--
At equilibrium	s+0.01	2s

The expression for  $K_{sp}$  of CaF<sub>2</sub> is:  $K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$

Substituting the values of  $K_{sp}$  and the equilibrium concentrations from the table we get

$$4.0 \times 10^{-11} = [s + 0.01][2s]^2$$

Assuming that the solubility is very low we ignore 's' in comparison to 0.01 M and write

$$4.0 \times 10^{-11} = [0.01][2s]^2 \Rightarrow 4s^2 = 4.0 \times 10^{-9} \text{ mol dm}^{-3}$$

$$\Rightarrow s^2 = 1.0 \times 10^{-9} \text{ mol dm}^{-3} \Rightarrow s = 3.16 \times 10^{-5} \text{ mol dm}^{-3}$$

As the value of solubility obtained is far less than 0.01 our assumption is valid.

In example, 9.7 we calculated the solubility of CaF<sub>2</sub> to be  $2.15 \times 10^{-4}$  M (in water) which was shown to decrease to about  $4.0 \times 10^{-7}$  M in presence 0.01 M sodium fluoride (example 9.8) i.e., about 525 times lesser.

Now we find that in presence of 0.01 M calcium nitrate the solubility has decreased to about  $3.16 \times 10^{-5}$  M which is about 7 times lesser than that in water.

This lesser decrease in case of calcium nitrate is due to the fact that in case of fluoride ion as the common ion the effect was significant because  $K_{sp}$  expression has second power of fluoride ion concentration whereas it depends on only the first power of concentration of calcium ions so the effect is marginal.

8. In order to arrange these salts in terms of increasing solubilities we need to calculate the solubilities of each of these salts separately.

MgF<sub>2</sub> is a salt of MX<sub>2</sub> type and from Table 9.2 the solubility is related to the  $K_{sp}$  as follows

$$s = \sqrt[3]{\frac{K_{sp}}{4}}$$

Substituting the value of  $K_{sp}$  we get,

$$s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{3.7 \times 10^{-8}}{4}} = 2.09 \times 10^{-3} M$$

$MgCO_3$  is a salt of MX type and from Table 9.2 the solubility is related to the  $K_{sp}$  as follows

$$s = \sqrt{K_{sp}}$$

Substituting the value of  $K_{sp}$  we get,

$$s = \sqrt{3.5 \times 10^{-8}} = 1.87 \times 10^{-4}$$

$Mg_3(PO_4)_2$  is a salt of  $M_3X_2$  type and from Table 9.2 the solubility is related to the  $K_{sp}$  as follows

$$s = \sqrt[5]{\frac{K_{sp}}{108}}$$

Substituting the value of  $K_{sp}$  we get,

$$s = \sqrt[5]{\frac{1.0 \times 10^{-25}}{108}} = 3.91 \times 10^{-6} M$$

Thus, the order of solubilities of the given salts is

